

CLAY MINERALOGY OF SOME OF THE PERMIAN SHALES

by

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TABLE OF CONTENTS

INTRODUCTION	1
Purpose of Investigation	1
Methods Used	1
REVIEW OF THE IMPORTANT LITERATURE	2
Shales	2
Clay Mineralogy	4
Clay Minerals in Marine Sediments	5
Bentonites	8
SAMPLING PROCEDURE	9
LABORATORY PROCEDURE	17
Separation of Clay Fraction from Shale Samples	17
Separation of Clay into Size Fractions by Use of the Supercentrifuge	19
Removal of Iron Oxide from Clays	22
X-ray Diffraction Analysis	24
X-ray Analysis with the Powder Camera	24
X-ray Analysis with the Geiger Counter Goniometer	26
Differential Thermal Analysis	27
CLAY MINERALOGY OF SOME OF THE PERMIAN SHALES	28
X-ray Identification of the Minerals in the Clay Size Range	28
Information Obtained by D. T. A.	32
Vertical Distribution of the Clay Minerals in the Permian Shales	39
Genesis of the Clay Minerals	47

INTRODUCTION

Purpose of Investigation

This investigation was concerned with the clay mineralogy of the upper Permian shales in the Manhattan area. Until recently there had been little work done in the study of clay minerals in shales. Most of the work on the clay minerals had been by agronomists while working with soils or by the mineralogist attempting to determine the atomic structure and crystalline character of the clay minerals.

While it was the purpose of this investigation to study all the clay minerals existing in the upper Permian shales of this area and to see if a relationship might exist between the physical appearance of the shale and the clay minerals present, this study was designed primarily to determine if a correlation exists between the chert-bearing limestones and the clay mineral composition of the shales underlying and overlying them. In previous work there has been evidence that volcanic ash is present in the chert-bearing limestones and that the clay mineral montmorillonite is more abundant in the shales underlying these limestones. If such a relationship does exist it would throw new light on the problem of the origin of chert.

Methods Used

Two of the most accurate analytical methods in determining the clay minerals present in a sample are differential thermal analysis

and X-ray diffraction analysis. The data gathered from differential thermal analysis complemented the information gained from X-ray diffraction and by using both methods a complete and accurate analysis of the clay minerals in a shale sample could be obtained.

REVIEW OF THE IMPORTANT LITERATURE

Shales

Shales represent the accumulation of the finest products of rock weathering. They are winnowed from the coarser, unsorted debris of weathering by geological agents.

To many people shales are merely hard, indurated clays. To the geologist, however, the term indicates a laminated sedimentary rock composed of finely divided mineral matter mostly of clay and silt size grade. The lamination is parallel to the bedding and has been developed during sedimentation and not by post depositional metamorphic action.

Shales can be classified by their detrital mineral composition or by their origin. Krynine (1948) classified the shales according to the detrital minerals present. In his classification he divided the shales into four different groups. The classification corresponds in mineral composition to the four main types of sandstone.

Krynine's classification is as follows:

- | | |
|--------------------|--|
| 1. Quartzose shale | quartz + chert |
| 2. Micaceous shale | quartz + chert + mica + chlorite
- feldspar |
| 3. Chloritic shale | quartz + chert + mica + chlorite
+ feldspar |

4. Kaolinitic or quartz + feldspar + clay
Feldspathic shale

Pettijohn's (1949) classification of the shales is by their origin. He divided them into two major groups, residual shales and transported shales. The residual shales are formed in place and are the product of soil forming processes. The transported shales derive the minerals and particles of which they are composed from three sources in varying proportions. The sources are the products of abrasion (mechanical clays), the products of weathering (residual clays), and by chemical addition.

The following is Pettijohn's genetic classification:

- I. Residual shales
- II. Transported shales
 - A. Residual products subordinate
 - 1. Graywacke shales
 - 2. Arkosic shales
 - 3. Tuffaceous shales
 - 4. Glacial shales
 - B. Residual products dominate (orthoquartzitic shales)
 - C. Chemical or organic components dominate
 - 1. Limy shales
 - 2. Sideritic shales
 - 3. Ferriferous shales
 - 4. Biopelites (black shales)
 - 5. Siliceous shales

Clay Mineralogy

Prior to about 1920 most workers in fields concerned with soils and clay materials held to one of two general concepts concerning the composition of the clay sized particles. One idea was that all of the clay sized material consisted essentially of one mineral, kaolinite. This was a natural mistake in as much as many commercial clay materials (porcelain clays) are nearly pure kaolinite in particles large enough for positive identification under the petrographic microscope. Most of the other clay minerals do not occur in particle size large enough for such identification. According to this belief the differences in chemical analysis of clay fractions from that of kaolinite were due to impurities.

A second view particularly popular with those studying soils from an engineering or an agronomic view point was that the essential clay component was an amorphous colloid complex. This was a justifiable and even useful misconception for those concerned with the dynamic and chemical aspects of clays. Nearly all clay minerals in the finer sizes easily form stable suspensions in water and the pronounced effects of the surface chemistry of all clay minerals often were seemingly explained by the same principles which were familiar to the colloidal chemist working with truly amorphous material. So well accepted was the colloidal concept that most of the debate on the subject was not as to the existence of colloids but as to the nature of the colloid which existed.

Defrénoy in 1856, Le Chatelier in 1887, and Lowenstein in 1909 were a few of the investigators that before 1920 believed the clays were not amorphous colloidal complexes, but consisted of a small group of minerals of definite structure and composition. For the most part the views of these men were based not on the observation of the clay minerals but on the fact that by their properties the clays could be easily classified, each having a rather definite performance. However, it was not until after 1920 when Hadding and Rinne working with X-ray diffraction, Ross, Shannon, and others of the U. S. Geological Survey using petrographic methods, and Marshall working with optical properties demonstrated the crystalline and mineral nature of the clays.

The work of Hadding and of Rinne is not only important because it helps to establish the crystallinity of the clays but also because it is the pioneer use of the X-ray diffraction technique in clay mineralogy. This method of analysis has not only made it possible for the positive identification of the clay minerals but even more important it has led to the determination of the crystal structure of the clay minerals.

Clay Minerals in Marine Sediments

Millot (1952) in his study of some rocks of marine origin presented evidence that the conditions of marine environment seemed to favor the formation of a montmorillonite, illite, or chlorite clay mineral rather than kaolinite. He found that the clay minerals of the mica type were predominate. Illite was the most abundant, followed

by the chlorite and hydrobiotite. Montmorillonite was rarely found and glauconite (ferric isotype of illite) did occur. Kaolinite was nearly always present but in small amounts and the amount of kaolinite decreased as the carbonate content increased. The presence of calcium ions in the sea water seemed to block the formation of kaolinite.

Grim, et al. (1949) have shown this also for recent marine sediments. In their study of some sediments from the Pacific Ocean they found that montmorillonite and illite were the most abundant clay minerals with chloritic material identified in some samples. There was a progressive decrease in the relative abundance of kaolinite away from the shore.

In the formation of clay minerals in a marine environment Grim (1953) seemed certain that chloritic mica and illite tend to form during marine diagenesis from other clay minerals. Thus illite probably forms from montmorillonite, chloritic mica tends to develop from kaolinite and possibly from montmorillonite. He also believes that the clay minerals could also be partly due to land derived muds carried to the sea. These muds consisting chiefly of degraded illites, kaolinites, and chloritic micas. Such degraded minerals have deficiencies of alkalies and alkaline earths and would quickly adsorb available potassium and magnesium from the sea water surrounding the sediments.

In the study of marine sediments that are Paleozoic or older the absence of the clay mineral montmorillonite has been noticed by many investigators. Murray (1954) in his study of the Pennsylvanian shales of Indiana and Illinois found that the material of clay size was composed almost entirely of four minerals, illite, kaolinite, chlorite,

and colloidal size quartz. Grim (1953) found in his analysis of ancient sediments that montmorillonite is generally absent in sediments older than the Mesozoic, except for a few beds that are probably of bentonitic origin. He explained this by reasoning that in the course of time, because of dehydration due to compaction, and the adsorption of potassium and magnesium from ground water, montmorillonite would tend to be altered in the direction of the micas.

During recent investigations, however, the presence of montmorillonite in sediments older than the Mesozoic has become more apparent. Swineford (1955) found in her study of the upper Permian rocks of Kansas, that the clays near the top of the section were chiefly montmorillonite. Hartig (1954) using differential thermal analysis and staining techniques found montmorillonite occurring above and below the chert bearing limestones in the Manhattan area. It was his belief that the montmorillonite was developed from volcanic ash.

The identification of mixed-layer clays in sediments has shown that montmorillonite in a mixed-layer with another clay mineral might occur in sediments older than the Mesozoic. Weaver (1956) in his examination of over 6,000 sedimentary rocks ranging in age from Cambrian to Recent, found that approximately 70 per cent or more of the samples contained some variety of mixed-layer clays. He also showed that the most common mixed-layer clays in sediments are composed of illite-montmorillonite, chlorite-vermiculite, and illite-chlorite-montmorillonite.

Bentonites

Bentonites have the physical property of swelling into a gelatinous mass or disintegrating into a granular or fluffy aggregate. They also have marked powers of adsorption.

The term bentonite has had several different definitions. Knight (1898) applied the term bentonite to a highly colloidal, plastic clay found in the Cretaceous beds of Wyoming near Fort Benton. In 1917 Hewett showed that bentonites were formed by the alteration of volcanic ash in situ. Later Ross and Shannon (1926) redefined the term bentonite to limit it to clays produced by the alteration of volcanic ash in situ.

Ross (1928) proposed the following definition for bentonite:

Bentonite is a rock term composed essentially of a crystalline, clay-like mineral formed by the devitrification and accompanying chemical alteration of a glass igneous material, usually a tuff or volcanic ash; and it often contains variable proportions of accessory crystal grains that were originally phenocrysts in the volcanic glass. The characteristic clay-like mineral has a micaceous habit and facile cleavage, high birefringence, and a texture inherited from volcanic tuff or ash, and it is usually the mineral montmorillonite but less often beidellite.

The process by which the volcanic ash is converted to bentonite has been the subject of much discussion. Hauser (1952) state that it had been shown many years prior, that montmorillonite could be produced by subjecting a synthetic glass as well as a natural obsidian to a high temperature and high pressure treatment. He said that it could be demonstrated that a devitrification phenomenon was involved

here in which the alumina and silica groups were rearranged under the influence of temperature and pressure to give a crystalline structure. He believed that the alteration was probably a combination of the chemical reactions attendant upon leaching and a devitrification of the glass. Probably the silica and alumina gels reacted first to form halloysite, then by condensation montmorillonite was formed.

Grim (1953) felt that in order for a bentonite to form it was probably necessary for the ash to fall into water. Since much of the bentonites are associated with marine formations, it was his belief that the alteration could easily take place in sea water. The composition of the ash also seemed to be important. Grim believed that the ash should have a moderate content of MgO , since ash devoid of magnesia did not seem to alter to montmorillonite. The alteration of the ash to montmorillonite seemed to take place soon after accumulation or possibly almost contemporaneously with accumulation.

SAMPLING PROCEDURE

Because any differences in the clay mineral composition within the individual shale units was to be determined in this investigation, linear serial samples were collected from shales outcropping in road cuts and ditches. Linear serial samples are a group of related spot samples collected in a line. Krumbein and Pettijohn (1938) defined a spot sample as an isolated sample taken at a particular point on the outcrop. The line of sampling was perpendicular to the plane of bedding. Samples were collected at the top and bottom of each shale unit

and then at equal intervals within each shale unit. The interval was determined by the thickness of the shale being sampled.

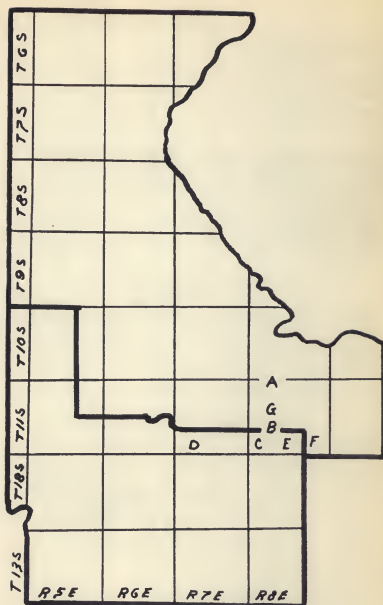
An area, about one foot square, on the outcrop face where the sample was to be collected was first cleaned or scraped so that all of the extraneous and weathered material was removed. Only the unweathered shale was used because clay minerals can be formed during the processes of weathering. A large piece of paper was then placed below the cleaned area and the unweathered shale chipped off with a pick onto the paper. The material on the paper was then emptied into a paper or cloth bag and properly labeled. The labeling consisted of a sample number, geographic locality, stratigraphic horizon, and the physical appearance of the shale.

The samples were collected along Kansas Highway Number 13 south of Manhattan in Riley County and along U. S. Highway Number 40 east of Junction City in Geary County. The stratigraphic units sampled were the shales of the lower Chase group, Wolfcampian series, Permian system to the upper portion of the Council Grove Group, Wolfcampian series, Permian system. The units sampled in the Chase group were the Blue Springs and Wymore shale members of the Matfield shale and the Havensville shale member of the Wreford limestone. The units that were sampled in the Council Grove group were the Speiser shale, Easley Creek shale, Hooser shale member of the Bader limestone, Stearns shale, and the Florena shale member of the Beattie limestone.

EXPLANATION OF PLATE I

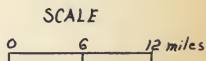
Map of Riley County and Geary County showing location of sampling sites.

PLATE I



EXPLANATION

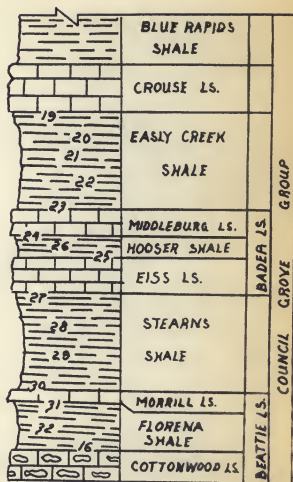
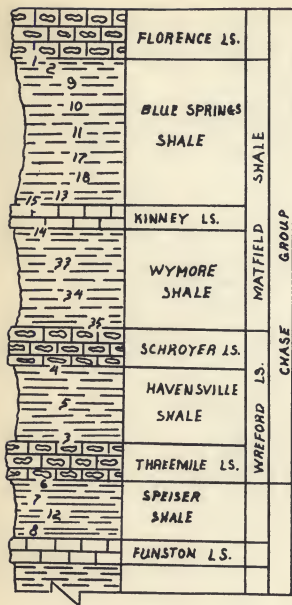
- COUNTY LINES
 ————— TOWNSHIP LINES
 A SAMPLING LOCATIONS



EXPLANATION OF PLATE II

Generalized stratigraphic section showing location of samples.

PLATE II



LEGEND



CHERTY LIMESTONE



LIMESTONE



SHALE

10

LOCATION OF SAMPLE

SCALE

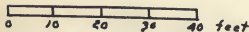


Table 1. Location of sampled units.

: Sample : Formation or number : member		: Geographic : Location : location on : in : Plate I : geologic section
1	Blue Springs shale	C At contact with overlying Florence limestone.
2	ditto	C One foot below Florence limestone.
3	Havensville shale	A At contact with the under-lying Threemile limestone.
4	ditto	A At contact with the over-lying Schroyer limestone.
5	ditto	A Middle of Havensville shale.
6	Speiser shale	A At contact with the over-lying Threemile limestone.
7	ditto	A At contact with overlying limestone in Speiser shale.
8	ditto	A Base of Speiser shale.
9	Blue Springs shale	B Five feet below the Florence limestone.
10	ditto	B Ten feet below the Florence limestone.
11	ditto	B 15 feet below the Florence limestone.
12	Speiser shale	D Middle of Speiser shale.
13	Blue Springs shale	E At contact with the under-lying Kinney limestone.
14	Wymore shale	E At contact with overlying Kinney limestone.
15	Blue Springs shale	E Thin seam of buff colored shale on top of Kinney limestone.

Table 1 (cont.)

Sample number	Formation or member	Geographic location on Plate I	Location in geologic section
16	Florena shale	F	At contact with underlying Cottonwood limestone.
17	Blue Springs shale	E	20 feet below the Florence limestone.
18	ditto	E	25 feet below the Florence limestone.
19	Easy Creek shale	F	At contact with the overlying Crouse limestone.
20	ditto	F	Five feet below Crouse limestone.
21	ditto	F	Ten feet below the Crouse limestone.
22	ditto	F	15 feet below the Crouse limestone.
23	ditto	F	At contact with the underlying Middleburg limestone.
24	Hooser shale	F	At contact with the overlying Middleburg limestone.
25	ditto	F	At contact with the underlying Eiss limestone.
26	ditto	F	Middle of Hooser shale.
27	Stearns shale	F	At contact with the overlying Eiss limestone.
28	ditto	F	Six feet below the Eiss limestone.
29	ditto	F	12 feet below the Eiss limestone.
30	ditto	F	At contact with the underlying Morrill limestone.

Table 1 (concl.)

Sample number	Formation or member	Geographic location : on Plate I	Location : in geologic section
31	Florena shale	F	At contact with the over-lying Morrill limestone.
32	ditto	F	Middle of Florena shale.
33	Wymore shale	E	Six feet below the Kinney limestone.
34	ditto	E	12 feet below the Kinney limestone.
35	ditto	G	At contact with the under-lying Schroyer limestone.

LABORATORY PROCEDURE

Separation of Clay Fraction from Shale Samples

One hundred grams of air dry shale were carefully weighed and placed in a Waring blender. For each 100 grams of sample 1 gram of sodium silicate was added along with approximately 400 cubic centimeters of de-ionized water. The samples were mixed in the blender for 15 minutes.

After the samples were removed from the blender they were washed over a U. S. series number 270 sieve to separate the sand from the silt and clay. The sand which was retained on the sieve was discarded.

The wash from the above separation which contained the silt and clay was transferred to a standard sedimentation cylinder and enough

de-ionized water added to bring the total volume to 1000 milliliters. The cylinders were placed in a constant temperature bath and allowed to stand several hours to reach the temperature of the bath (20° C.).

Each of the samples was then shaken by hand for one minute and replaced in the bath to allow settling of the silt sized particles. The samples were allowed to stand eight hours for each ten centimeters of settling distance with an additional 50 per cent settling time allowed for the first separation.

A total of 30 centimeters of suspension was siphoned from the upper part of the sedimentation cylinder after 36 hours of settling time. The siphoned material containing the clay sized particles was placed in a four liter jug and the sedimentation cylinders containing the settled particles were refilled to 1000 milliliters with de-ionized water, reshaken for one minute by hand and again set back in the temperature bath for 24 hours more. After the 24 hours had elapsed the upper 30 centimeters of suspension were again siphoned into a four liter jug. Two separations were all that was necessary in obtaining a sufficient amount of clay for analysis.

Oriented aggregates of the clay minerals were then prepared by putting some of the suspension from the jugs on a glass microscope slide with an eye dropper. The suspension was allowed to dry on the microscope slide under room conditions. When the suspension had dried a thin film of clay minerals was left oriented on the microscope slide. Clay minerals oriented in this way give only the basal reflections in X-ray diffraction analysis.

The clay was flocculated out of suspension in the jugs by the addition of hydrochloric acid until the suspension reached a pH of 3.5. After flocculation had taken place the clear liquid was decanted. The remainder of the clay suspension left in the jugs was vacuum filtered through a Buechner funnel using Whatman number 42 filter paper. The residue was air dried and crushed with a mortar and pestle and placed in a glass vial. Sample numbers were marked on the glass vials with a grease pencil. The clay sized material in the vials was to be used in differential thermal analysis and for film techniques in X-ray powder diffraction.

Separation of Clay into Size Fractions by Use of the Supercentrifuge

According to Jackson (1950) the best size limits of the segregation of the clay minerals are between 2 and 0.2 micron, 0.2 micron and 0.08 micron, and less than 0.08 micron.

The separation of the size fractions of the clays was accomplished by using a Sharples laboratory model air-turbine supercentrifuge equipped with a clarifier bowl having a removable cellulose liner. The removable liner was used to facilitate cleaning the bowl after each separation.

Separations at the 0.08 micron limiting diameter were made first. For this size a supercentrifuge bowl speed of 25,000 revolutions per minute and a suspension flow rate of 106 milliliters per minute was used. The 25,000 revolutions per minute speed required an air pressure of 11 to 12 pounds per square inch. The suspension was fed to the

supercentrifuge at a constant rate by using two feed reservoirs one above the other. The lower reservoir consisted of a glass funnel connected to the feed nozzle of the supercentrifuge by a rubber tube. The upper reservoir consisted of a glass cone blown percolator capable of holding 4500 milliliters of suspension and was located directly above the lower reservoir. A screwcock on the tube from the upper reservoir made it possible to maintain a constant suspension level in the lower reservoir. Pinchcocks were used on the rubber tubes of both the upper and lower reservoirs to stop the flow when necessary.

The feed rate of 106 milliliters per minute was obtained by using the small feed nozzle for the supercentrifuge and adjusting the height of the lower feed reservoir. The necessary height was found by experiment to be 46 inches measured from the top of the suspension in the lower reservoir to the top of the table on which the supercentrifuge rested.

Prior to beginning a separation the suspension was placed in a Waring blender and mixed for 15 minutes. While the suspension was being mixed the supercentrifuge was started and brought to a speed of 25,000 revolutions per minute. After this speed was attained a flow of de-ionized water was fed into the supercentrifuge from the feed reservoirs. The initial flow of water caused the speed to be somewhat reduced but it was regained after a few minutes. When the proper speed was reattained the clay suspension was taken from the blender and emptied into the upper reservoir. The lower reservoir was filled to the proper level from the upper reservoir and then the suspension was fed into the supercentrifuge from the lower reservoir and a constant

level maintained in the lower reservoir by adjusting the screwcock on the upper reservoir.

The effluent from the supercentrifuge which was collected in a four liter jug contained most of the less than 0.08 micron material. The greater than 0.08 micron material and part of the less than 0.08 micron material was deposited on the cellulose liner during the centrifuging process. Just before the upper reservoir was drained its sides were washed down with de-ionized water. Then about 300 milliliters of de-ionized water was poured into the upper reservoir and held there until the lower reservoir was nearly empty. The water from the upper reservoir was then fed into the lower reservoir and on into the supercentrifuge to displace the suspension remaining in the bowl. When the water had been emptied from both reservoirs the air pressure was turned off and the bowl allowed to coast to a stop. Breaking action was considered undesirable as it would cause loosening of some of the particles from the cellulose liner and subsequent loss of those particles.

The less than 0.08 micron material was flocculated out in the jugs by raising the pH to 3.5. The clear solution was then decanted and the remainder vacuum-filtered using Whatman number 42 filter paper.

After the bowl had coasted to a stop it was removed from the supercentrifuge and the cellulose liner taken from it. The sedimented particles on the liner were transferred from the cellulose liner to the Waring blender and de-ionized water added. The suspension was allowed to mix for 15 minutes prior to its second separation at the 0.08 micron limit. The same procedure was followed on the succeeding

separations which were made until the effluent from the supercentrifuge was clear, usually requiring four or five separations.

The separations at the 0.2 micron limit were made just like those at the 0.08 micron limit except that the required feed rate was 415 milliliters per minute. This rate was attained by using the medium feed nozzle on the supercentrifuge along with a lower reservoir height of $30\text{-}3\frac{3}{4}$ inches.

Removal of Iron Oxide from Clays

It was found, when using powder camera techniques of X-ray diffraction with nickel filtered copper radiation, that the clays with iron oxide present in them would give a background so dark that the diffraction lines on the film could not be interpreted. This difficulty was not encountered when using oriented aggregates and direct measurement techniques of X-ray diffraction. Since in the preliminary part of this investigation powder camera techniques of X-ray analysis were used it was necessary to use some method of iron oxide removal that would not destroy the clay minerals. One of the easiest ways to remove the iron oxide is using hydrochloric acid to dissolve the iron oxide. It was feared that the use of hydrochloric acid in this investigation would alter or dissolve some of the clay minerals present. It is known that the montmorillonoids are especially soluble in hydrochloric acid.

The method that was chosen was one which is similar to the method described by Barshad (1954). In this method a citrate reagent and a dithionite reagent were used. The citrate reagent was prepared by

dissolving approximately 75 grams of tribasic sodium citrate in 900 milliliters of warm water, then adding five molar solution of citric acid until a pH of 7.3 was reached. The solution was then brought to a total volume of 1,000 milliliters. The dithionite reagent was prepared by dissolving one gram of sodium hydrosulfite in about five milliliters of distilled water for each sample treated. The solution was mixed and the pH brought to 7.3 by means of a few drops of 10 per cent sodium hydroxide.

It is possible to dissolve about 0.5 gram of Fe_2O_3 in 40 milliliters of the citrate reagent. Thus a ten gram sample of 5 per cent extractable Fe_2O_3 could be treated with one 40 milliliter portion of the citrate reagent.

In the removal of iron oxide a sample with 0.5 gram of extractable Fe_2O_3 or less, was placed in a 100 milliliter centrifuge tube and 40 milliliters of citrate reagent added. The temperature was increased to 80 or 90° C. in a water bath and then the dithionite solution added and the mixture stirred continuously for five minutes and occasionally for ten minutes longer. Near the end of the digestion, ten milliliters of saturated sodium chloride solution was added to the suspension, stirred, and allowed to digest for one minute. The suspension was centrifuged for five minutes at 2,200 revolutions per minute and the supernatant liquid decanted. For samples which originally contained less than five per cent extractable Fe_2O_3 the treatment was repeated. For samples containing 5 per cent or more three treatment were necessary. A final treatment was made consisting of washing the sample with the citrate solution. The sample was then washed three times with 75 per

cent acetone and once with 100 per cent acetone.

X-ray Diffraction Analysis

X-ray diffraction essentially involves two components, the X-ray unit and some method of recording the diffracted rays. Recording the diffracted rays may be accomplished by use of a properly sensitized photographic film or by the more modern method of a geiger counter goniometer and a strip chart recorder. Both recording methods were used in this investigation. The photographic film technique was employed in the preliminary part of the investigation and during the rest of the study the geiger counter goniometer with a strip chart recorder was used.

In operation, a beam of X-rays is directed into the sample which is to be analyzed. This causes a series of secondary beams to be emitted from the specimen in the form of a cone. Analysis of this cone with a photographic film shows a series of diffraction lines in the form of concentric circles. The lines occur as a result of the cancellation and reinforcement of the reflections from various atomic planes of the specimen. The film with the diffraction lines recorded on it is termed an X-ray pattern, and no two different materials have ever been found which show identical patterns. This means that X-ray diffraction is a positive means of identification.

X-ray Analysis with the Powder Camera. After the sample had been treated to remove the iron oxides it was thoroughly ground in a mortar and pestle. One small portion of the ground sample was then separated

from the rest and treated with glycerol for aid in the identification of montmorillonite. Using two pieces of glass part of the untreated sample was then pressed into a wedge shaped sample holder of an X-ray camera. The remainder of the untreated sample was placed in a container for later use. The portion of the sample that was treated with glycerol was also pressed into a wedge shaped sample holder of another camera. The sample holders were then placed in their respective cameras and adjusted so that the radiation would strike only the upper part of the sample (the thin edge of the wedge). The adjustment was made by looking through the slit system and raising or lowering the sample holder until it covered half of the opening.

The cameras were placed on the X-ray unit and exposed to nickel filtered copper radiation, using 20 milliamps and 40 kilovolts, for five hours. After the exposure time had elapsed the X-ray unit was turned off and the cameras removed. The film from each camera was placed in a developing solution and allowed to remain there for eight minutes. The films were then washed with water and placed in the hypo bath and left for 18 minutes. After removing the films from the hypo bath, both were washed thoroughly with water and allowed to dry. When the films had dried the diffraction lines were measured and the angular spacings calculated by using the formula $d \sin \theta = \lambda$, where d is the linear distance, measured on the film in centimeters, from the diffraction line to the point where the incident beam strikes the film; and θ is the Bragg angle in degrees. After the angular spacings had been calculated they were converted to d-spacings, measured in angstrom units, by using the "Tables for Conversion of X-ray Diffraction Angles to Interplanar Spacing." The measured d-spacings were

then compared with both the theoretical and measured d-spacings of minerals in the clay size range to determine what minerals were present.

X-ray Analysis with the Geiger Counter Goniometer. Oriented aggregates of the clay minerals on microscope slides, which had been prepared previously, were placed in the slide holder of a North American Phillips diffraction unit. The specimen was then exposed to nickel filtered copper radiation, utilizing 20 milliamps, 40 kilovolts with a one degree slit system, a rate meter scale factor of eight, and a time constant of four seconds. Scanning speed of goniometer was $1/4$ degree two theta per minute. The geiger counter goniometer was run from 30 degrees two theta to four degrees two theta. After this run was completed the oriented sample was treated with ethylene glycol. The glycol was added by spraying it on the sample with an atomizer. The effect of the glycol was to form an organic complex with montmorillonite and cause it to expand. Montmorillonite will expand its basal spacing to 17.7 angstroms when ethylene glycol is added, this made it much easier to recognize montmorillonite in the samples. After the sample had been treated with glycol it was again exposed to nickel filtered copper radiation and the geiger counter tube was run from 14 degrees two theta to four degrees two theta. This angular distance would include the (001) and (002) chlorite and vermiculite peaks, the (001) peak of illite, kaolinite and of montmorillonite in its expanded position.

After completing the second run the angular spacings, which were recorded directly on the strip chart in degrees two theta, were

converted to d-spacings. This conversion was made by again using the "Tables for Conversion of X-ray Diffraction Angles to Interplanar Spacing". The d-spacings were compared with the theoretical and measured d-spacings of minerals that might be found in the clay size range. The diffraction line profiles were studied to determine the condition of the clay minerals.

It was found that using oriented aggregates and the geiger counter goniometer with a strip chart recorder gave much more information than the powder camera method. Part of the reason for this is the fact that the strip chart recorder plots diffraction line profiles. The positions of the diffraction lines and their profiles will tell much about the clay minerals present. They will give clues as to the type of clay minerals in the sample and to the condition the clay minerals are in; i.e., if the clay minerals are well crystalline, degraded, or in a mixed-layer form; whereas with the powder camera, only the types of clay minerals can be determined.

Differential Thermal Analysis

The method of differential thermal analysis is essentially that of heating the sample at a constant rate of increase of temperature up to 1,000° C. While the sample was being heated at an increasing temperature the thermal reactions were measured. These thermal reactions occur by the comparison of the temperature of the sample with that of a similarly heated thermally inert substance such as calcined aluminum oxide, which was used in this investigation. The sample, after being

ground to a fine powder with a mortar and pestle, was placed in one hole of a specially constructed nickel specimen holder and the calcined aluminum oxide in another hole. The heating rate was determined by a thermocouple placed in the nickel block just below and between the holes which held the sample and the aluminum oxide. The thermal reactions were measured by means of a differential double-junction thermocouple, one junction was inserted in the sample being analyzed and the other junction was in the thermally inert aluminum oxide. Both measurements were recorded automatically in the form of plotted curves by the use of Leeds and Northrup micromax recorders. The heating element of the Hoskins Hevi-duty oven in which the samples were heated had been modified to allow a higher heating rate than is generally used with these ovens.

The effectiveness of differential thermal analysis in the determination of clay minerals is the result of differences in intensities of these reactions. Thus each mineral shows a characteristic curve upon heating. By direct comparison of the curves of an unknown sample with the thermal curves of pure clay minerals that might occur in the unknown sample, the clay mineral composition can often be determined.

CLAY MINERALOGY OF SOME OF THE PERMIAN SHALES

X-ray Identification of the Minerals in the Clay Size Range

The analysis of complex clay mineral mixtures such as those occurring in the upper Permian shales of the Manhattan area present many

difficult problems in the interpretation of X-ray diffraction data. The problems become even more complex when a quantitative estimate is made of the clay minerals.

Most of the material in the clay size range of the shales is composed of illite, chlorite, colloidal quartz, colloidal calcite, and mixed-layer clay minerals of montmorillonite-illite, chlorite-vermiculite, and chlorite-illite. All of the clay minerals, except chlorite, are three-layer type silicates. Chlorite is a regularly mixed-layer type with ordered stacking of alternate layers of different types.

X-ray diffraction data was obtained from oriented aggregates before and after treatment with ethylene glycol, after heating to 450° C. to remove poorly crystalline chlorite, and after the sample had been heated to 600° C. to remove kaolinite. The treatments with ethylene glycol and heating aided greatly in the identification of the clay minerals present.

Illite was identified as a constituent of the shales on the basis of the 10-A basal reflection and other basal reflections with a 10-A periodicity. These reflections remained unchanged after treatment with ethylene glycol. Illite was found to be the predominate clay mineral in all of the samples investigated.

The identification of chlorite as one of the clay minerals present in the samples was based primarily on the integral series of orders related to a 14-A periodicity which remained unaltered following glycolation. To distinguish chlorite from kaolinite (both of which have two basal reflections in common, the second and fourth orders of chlorite and the first and second orders of kaolinite occurring at 7-A and 3.5-A

respectively) the diagnostic first and third order reflections of chlorite occurring at 14-A and 4.7-A were used. In many cases the 4.7A reflection of chlorite appeared only as a modification of the symmetry of the 5-A reflection of illite. Using this type of analysis it was impossible to determine the amounts of kaolinite mixed within the chlorite or within other clay minerals.

The two non-clay minerals that were found in the clay size range, quartz and calcite, were identified by the 4.2-A reflection of quartz and the 3.03-A reflection of calcite. It was also by use of these two reflections that the relative amounts of the two minerals were obtained.

The similar structural basis of most of the clay minerals leads to the possibility of mixed-layer structures, in which layers of different types alternate. Two of the most common ways for such mixtures to occur are: (1) existence of two different degrees of hydration, i.e., a mixture of mica-type layers with montmorillonoid or vermiculite type of layers; and (2), to have brucite layers mixed with mica-type layers, or layers of water molecules; i.e., in mixed chlorite-vermiculite structures. There are three different ways in which the mixed-layers may be distributed, however, only two of these were found in this investigation, the regularly mixed-layers and randomly mixed-layers.

Mixed-layer structures give reflections that are averages of the reflections of the component clay minerals in the mixture. By determining if the reflections form an integral series or not it is possible to decide if the structure is regularly or randomly mixed. If the structure is a regularly mixed-layer type it will give a high

spacing reflection and a series of sharp higher order reflections with spacings which are sub-multiples of the high spacing reflection. If, however, the mixture is of the random type the reflections will give spacings which do not form an integral series, also the random structure will give a marked rise of scattering near the primary beam.

Identification of a mixed-layer chlorite-vermiculite in the shales was based on the presence of a 14-A spacing that would expand to about 15.5-A after treatment with ethylene glycol. The chlorite-vermiculite was found to be predominantly a randomly mixed-layer structure, however, in a few cases there was evidence that the structure was a regularly mixed-layer clay. Of the mixed-layer structures found, only the chlorite-vermiculite ever showed evidence of being regularly mixed.

The chlorite-illite mixed-layer present in the samples showed a characteristic reflection which was the average of the 14-A first order basal spacing of chlorite and the 10-A first order basal spacing of illite. This average reflection varied from about 11-A to 12.8-A depending upon the amount of chlorite or illite present. Also this spacing would not expand upon treatment with ethylene glycol.

The final mixed-layer structure identified was montmorillonite-illite. It was recognized by the symmetry of the 10-A reflection of illite. The 10-A reflection of illite was quite asymmetrical before glycolation, but after the sample had been treated with ethylene glycol the 10-A reflection became quite symmetrical and showed a marked decrease in intensity. The change in profile of the 10-A peak is believed to be caused by the expansion of the montmorillonite upon the addition of the ethylene glycol. An average reflection due to a

montmorillonite hydrated with one layer of water and an illite would give a spacing that could vary from 12.4-A (pure montmorillonite) to 10-A (pure illite). This spacing might only show as an effect on the symmetry of the 10-A illite peak if there should be a lack of resolution. The relative amount of montmorillonite was determined by the asymmetry of the 10-A peak, the more asymmetrical the peak the more montmorillonite there was present. This method of estimation is subject to error in that there are other reasons which might produce an asymmetrical 10-A illite peak, i.e., a degraded illite or a small amount of chlorite mixed with illite. However, since the peak became almost perfectly symmetrical after glycolation it was considered that the asymmetry was due largely, if not entirely, to montmorillonite.

Plate III shows the 10-A illite peak of two typical samples containing montmorillonite before and after treatment with ethylene glycol. Plate III also shows the expansion of the 13.7-A mixed-layer chlorite-vermiculite spacing to 15.5-A after treatment with ethylene glycol. The 10-A illite peak shown on Plate IV is one without any montmorillonite interlayered with illite.

Information Obtained by D.T.A.

Differential thermal data was obtained for many of the samples. All the samples showed endothermic reactions between 100° C. and 200° C. caused by the loss of interlayer or adsorbed water. Following this reaction were endothermic reactions occurring between 600° C. to 700° C. (loss of OH or lattice water), 800° C. to 900° C. (final breakdown

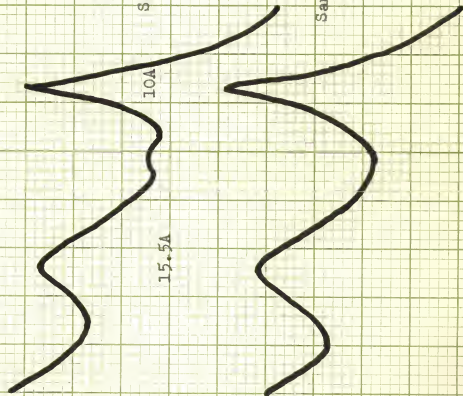
EXPLANATION OF PLATE III

X-ray spectrometer tracings of samples containing montmorillonite, showing the change in the symmetry of the 10-A peak after treatment with ethylene glycol. The Plate also shows the shift of the 13.7-A peak to 15.5-A after treatment with ethylene glycol.

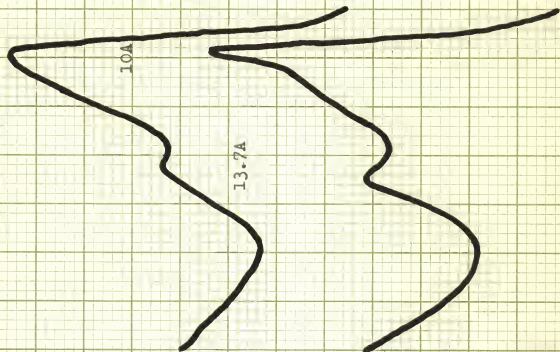
PLATE III

WITH ETHYLENE GLYCOL

WITHOUT ETHYLENE GLYCOL



Sample 4



Sample 5

EXPLANATION OF PLATE IV

X-ray spectrometer tracing of a sample which contains no montmorillonite, showing that the 10-A peak does not change symmetry upon treatment with ethylene glycol. The Plate also shows the shift of the 14.2-A peak to 15.5-A after treatment with ethylene glycol.

PLATE IV

WITH ETHYLENE GLYCOL

WITHOUT ETHYLENE GLYCOL

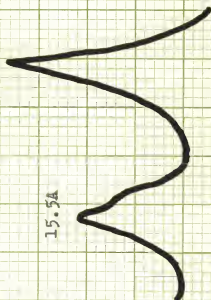
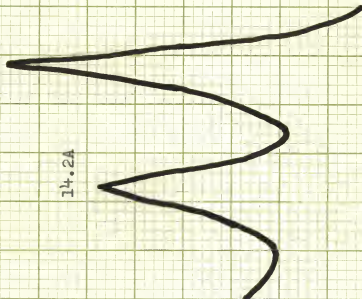
10A

14.2A

10A

15.5A

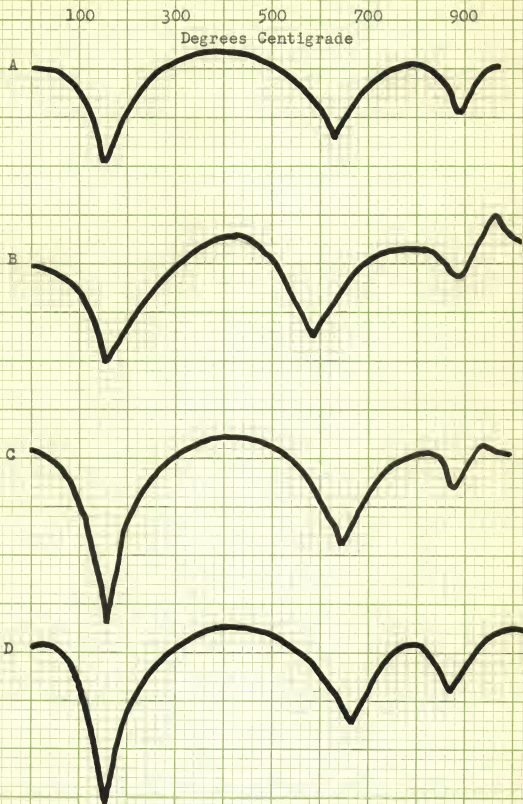
Sample 24



EXPLANATION OF PLATE V

Differential thermal analysis (D.T.A.) curves.

- A. D.T.A. curve of sample 21 showing characteristic illite reactions.
- B. D.T.A. curve of an illite clay sample from Grim (1953) p. 197 showing characteristic endothermic peaks at 100°-200° C., 500°-600° C., and about 900° C.
- C. D.T.A. curve of sample 19 showing montmorillonite reactions.
- D. D.T.A. curve of a montmorillonite clay sample from Grim (1953) p. 198, showing characteristic endothermic peaks at 100° C.-250° C., and between 600°-700° C.



of the crystal lattice), and exothermic occurring at about 900° C. (formation of spinel). The endothermic reactions occurring between 100° C.-200° C., and 600° C.-700° C., showed a relationship to the amount of montmorillonite as determined by X-ray diffraction. As the amount of montmorillonite increased in the samples the temperature of these reactions tended to increase. This should be expected since a mixed-layer might give thermal reactions which would occur somewhere between the thermal reactions of the pure minerals which compose the mixed-layer. The reactions would also probably increase or decrease in temperature as the relative amounts of the two clays increased or decreased.

Some of the D.T.A. curves showed characteristic thermal reactions which might be correlated with well crystalline chlorite. They also quite often showed the presence of a carbonate, probably calcite.

Vertical Distribution of the Clay Minerals in the Permian Shales

The clay mineral composition of the upper Permian shales in the Manhattan area showed many interesting relationships. From these correlations the environmental conditions can often be determined.

An analysis of the samples indicates that more montmorillonite occurs in the shales directly above and below the chert-bearing limestones than occurs in the shales that are not associated with cherty limestones. The samples collected in the Blue Springs shale shows more montmorillonite to be present directly under the Florence limestone with a general decrease in the amount of montmorillonite near

the middle of the shale unit. The montmorillonite content begins to increase again near the Kinney limestone. This same general trend is found in the Wymore shale, montmorillonite decreasing toward the middle of the rock unit and increasing approaching the Schroyer limestone. In Havensville shale, which has cherty limestones both above and below it, the montmorillonite content remained high and constant. Again in the Speiser shale the amount of montmorillonite decreased progressively farther away from the Threemile limestone. The amount of montmorillonite in the Easley Creek shale shows a decrease away from the Crouse limestone. In the Hooser and Stearns shale the montmorillonite content remained low without much variation, however, in the Florena shale the amount of montmorillonite increased nearer the Cottonwood limestone.

There were only two limestones which showed an abundance of montmorillonite in the shales directly above and below them which were not always chert bearing, the Crouse and the Kinney. The Crouse limestone contains chert only in certain local areas and the Kinney limestone is non-chert bearing. However, volcanic glass shards have been found in the Kinney limestone.

In many cases the clay mineral composition showed a relation to the color of the shale. The red shales showed calcite to be one of the predominant minerals in the clay size range. There was also evidence that kaolinite might be present. The presence of kaolinite was based on indirect evidence. It was found that the 7-A peak, which could be caused by either chlorite or kaolinite, or both, was very intense. If this peak was due only to chlorite it would indicate an abundance of this mineral. However, upon examining the relative

amounts of chlorite in mixed-layer form with vermiculite and with illite it was found to be the minor constituent in both cases. It would appear that if there was an abundance of chlorite formed during diagenesis of the clay minerals it should also be the major constituent of the mixed-layer clays present. Since this was not the case and the 4.7-A reflection of chlorite was quite weak or entirely absent it was assumed that part of the 7-A reflection was caused by kaolinite.

The characteristic minerals in the clay size range of dark gray and gray shales were chlorite, and of course illite. The intensities of the 14-A, 7-A, 4.7-A, and 3.5-A reflections were all quite high, indicating that chlorite was a major constituent. The mixed-layer clay chlorite-vermiculite was found to be present in every sample of gray shale, and chlorite was always the more abundant component. Quartz was found to be a minor constituent, usually varying from minor to absent. The rest of the minerals in the clay size range were of variable proportions in the gray shales.

No correlation could be found between the color of the green and yellow or buff shales with their clay mineral composition. This might be expected of the green shales since the reduction of any of the iron compounds present might cause a green color and might have little or no effect on the clay minerals present.

Chlorite and quartz seem generally to bear a reciprocal relation to one another. Although this was not the case in every sample that was analyzed, the general trend of the amount of the two minerals seemed to indicate that as the amount of chlorite increased the amount

of quartz would decrease, and vice versa.

Interstratified chlorite-illite clay minerals were not found in every sample. In the samples in which they were recognized there appeared to be no relation between the presence of such a mixed-layer clay and the physical appearance or stratigraphic horizon of the shales. The composition of these mixed-layer structures would vary from 50 per cent chlorite-50 per cent illite to 20 per cent chlorite-80 per cent illite.

In all of the shales, with the exception of the Havensville, the clay mineral composition would change at different vertical locations within the individual shale unit. The mineral composition in the clay size range of the Havensville, however, remained constant throughout the vertical extent of the shale. It appears that the entire Havensville shale was deposited under constant environmental conditions.

The quartz in the clay size range showed a general tendency to be more abundant in the shales directly above and below the chert-bearing limestones than in any other stratigraphic horizon. It was only in the Florena shale directly above the chert-bearing Cottonwood limestone that this relationship did not hold. But the Florena shale does show abundant silicified fossils.

The clay size calcite was generally most abundant in the red shales, but still a very minor constituent overall. Whenever a red shale was analyzed, calcite was always an abundant to a major constituent in the clay size fraction of the shale. This would seem contradictory when it is realized that it was only in the red shales that any evidence of kaolinite existed, and the presence of calcite presumably

blocks the formation of kaolinite. This can be explained by reasoning that even though the amount of calcite in the clay size range is relatively large the total amount of calcite present in the entire shale may be quite small. Another explanation might be that the kaolinite did not form in place, but represents a transported clay mineral which was not completely altered by the marine environment.

An interesting observation connected with the presence of calcite in the clay size fraction of shales is that the red shales are not calcareous megascopically in spite of the fact that they do have a considerable amount of calcite in the clay size range, whereas the other shales are calcareous and have a variable amount of calcite in the clay fraction, ranging from a major constituent to entirely absent.

Table 2. Summary of the clay minerals present in the shales.

Geologic section :	Color :	Illite :	Chlorite :	illite :	Chlorite- : vermiculite :	illite- : Chlorite- : C/V :	Montmor- : illite :	Quartz : Calcite
Florence limestone (cherty)								
	Gray	Major	Abundant	P	P	P	P	Abundant Minor
	Green	Major	Minor		P			Major
	Red	Major	Abundant + kaolin (?)	P		P		Abundant Major
	Green	Major				P		Minor
	Green	Major	Abundant	P	P			Abundant Minor
	Gray	Major	Major	P	P		P	Abundant Abundant
	Gray	Major	Major		P		P	Trace Minor
Kinney Limestone (contains volcanic glass shards)								
	Buff	Major	Major		P		P	Abundant Minor
	Buff	Major	Major	P	P			Abundant Major
	Buff	Major	Minor		P			Trace Major
	Buff	Major				P		Minor Major
Schroyer limestone (cherty)								
	Buff	Major	Minor		P		P	Minor
	Gray	Major	Minor		P		P	Trace

Havens-
ville
Shale

Table 2. (cont.)

Geologic section :	Color :	Illite :	Chlorite :	illite :	Chlorite- : Chlorite- :	vermiculite :	illite- :	Montmor- :	Quartz :	Calcite :
Havensville shale	Buff	Major	Trace		P	P	P		Minor	
Threemile limestone (cherty)										
	Buff	Major	Trace	P	P	P	P		Minor	
Spelter shale	Red	Major	Minor + kaolin (?)		P	P	P		Abundant	
Funston limestone	Buff	Major			P					
Blue Rapids shale										
Crouse limestone (locally cherty)										
	Buff	Major		P	P		P		Abundant	Trace
	Buff	Major	Minor	P	P	P	P		Trace	Trace
	Green	Major	Abundant	P	P	P	P		Abundant	
	Red	Major	Minor + kaolin (?)	P	P	P	P		Major	
Early Creek shale	Buff	Major	Minor	P	P	P	P		Trace	

Genesis of the Clay Minerals

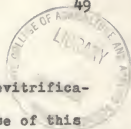
There are two theories which are the most prevalent for the origin of clay minerals. The "residual clay" and the "transported clay" theories. The residual clay idea suggests the origin of clay minerals as a result of surface weathering of fresh rocks, or by the action of solutions, whereas the transported clay theory postulates that the residual clays were carried by rainwash into streams and were then transported to other locations where the clays were finally deposited.

The origin of the clay minerals in upper Permian shales of the Manhattan area probably cannot be explained by one simple method of formation. It is more likely that when discussing the origin of these clay minerals both theories should be kept in mind.

It is the author's opinion that the montmorillonite that is associated above and below the chert bearing limestones represent altered volcanic ash. Markley (1953) and Hartig (1954) have shown the presence of volcanic glass shards in the chert bearing limestones. This ash was probably deposited in shallow marine waters with silt and clay and underwent a devitrification process to form montmorillonite. Hauser (1952) stated that such a process can occur and has been artificially produced in the laboratory. According to Grim (1953) the best conditions for the formation of montmorillonite from ash is for the volcanic ash to have a moderate content of magnesia and to be deposited in marine waters. The source of the volcanic ash for this area might well have been from the volcanic arch which in Permian time

bordered what is now the coast of California. According to Eardley (1951) the volcanic rocks of Permian age along the California coast are mostly andesites and basalts. If this is the case, then the ash falls which would accompany the eruptions that produced these rocks would probably be intermediate to basic in chemical composition and therefore contain at least a moderate amount of magnesia. This volcanic ash then being deposited in the marine waters which covered this area in Permian time would have all the favorable conditions for the alteration to montmorillonite. Grim (1953) believed that the alteration of ash to montmorillonite is almost contemporaneous with accumulation. Not all of the montmorillonite was formed in this way. Since the marine environment favors the formation of montmorillonite, its presence may be due in part to other methods of origin, such as the leaching of potassium out of illite. It would appear that with so many favorable conditions for the formation of montmorillonite it should be much more abundant in the Permian shales. However, Grim (1953) explained that due to metamorphic processes montmorillonite would alter to a mica type clay mineral and therefore tend to disappear in ancient sediments. These same processes could also form a mixed-layer montmorillonite-illite quite easily. If not enough time had elapsed for the montmorillonite to be completely altered to a mica type clay mineral such as illite, there would probably be layers of illite and montmorillonite interleaved with one another.

The presence of montmorillonite, presumably formed from volcanic ash, in the shales directly above and below the chert bearing limestones and limestones containing volcanic glass shards would indicate



that the formation of chert might be associated with the devitrification of volcanic ash. However, since it was not the purpose of this thesis to attempt an explanation for the origin of chert in this area, nothing more need be said than that a relationship does exist between the chert bearing limestones and the montmorillonite content of the shales directly above and below them.

The reciprocal relationship that exists between chlorite and quartz in the clay size fraction seems to indicate that when the marine environment favors the formation of chlorite most of the colloidal quartz would be used in its formation. According to Glass (1952) a relatively high chlorite content would indicate a brackish water environment. He also says that micaceous materials are dominant in a non-reducing marine environment and the glauconite-montmorillonite series becomes higher in a reducing marine environment. Glauconite is the ferric isotype of illite. Rowland (1952) felt that if chlorite was formed by the precipitation of magnesium hydroxide between the layers of a fragmentary montmorillonite-like mineral, such as vermiculite, its presence would indicate a silica-poor, reducing environment. Since chlorite and the mixed-layer chlorite-vermiculite are abundant in the gray shales in this area, it would appear that the deposition of these gray shales took place in oxygen-poor, brackish water.

The kaolinite present in the red shales in this area is either allochthonous or due to weathering upon exposure to the atmosphere. Kaolinite is chiefly a weathering product and is not generally formed in a marine environment. The predominance of illite in these red shales indicates that the shales probably did accumulate in sea water. Illite

is a clay mineral which is easily formed during marine diagenesis of the clay minerals. The red shales of the Manhattan area, then, might represent the accumulation of transported clay materials in a shallow sea where oxidizing conditions were predominant, or, they may be due to a short time exposure of previously deposited sediments to the atmosphere. According to Pettijohn (1949) red shales originate under intermittently rainy, subarid or arid climates without any close relation to temperature. He believed that they are typically fluvial or pluvial deposits upon land, though to a limited extent they could be fluviated deposits coming to rest on the bottom of a shallow sea.

In all the shales illite was the predominant mineral in the clay size range. If the shales were deposited in a marine environment this is to be expected since illite is the characteristic clay mineral produced in a marine environment. The illite present could have been formed by the slow alteration of montmorillonite under marine conditions. It also might represent a degraded mineral present in land derived muds which were carried to the sea. Degraded illites are illites which have been leached of their constituent alkalis and alkaline earths, but not sufficiently to transform them into new minerals. The degraded illites would then adsorb available potassium to complete their mica type structure. The illite in mixed-layer with montmorillonite was probably formed by compression acting on the montmorillonite and altering part of it to illite in a marine environment.

Mixed-layer clays of chlorite-illite could have been produced by the precipitation of magnesium hydroxide between the layers of montmorillonite and then by compression to form the illite present.

Another explanation might be that degraded illites in adsorbing potassium to complete their structure would also adsorb enough magnesium to produce small amounts of chloritic mica.

The chlorite which is not in mixed-layers with other minerals probably originated in several different ways. It might occur by filling all of the exchange positions in montmorillonite with magnesium. Chlorite could also be formed by the alteration of kaolinite in a marine environment, or it could be produced from land derived muds carrying large amounts of degraded clay minerals that were deposited where there was an excess of magnesium present. Chlorite might also be detrital.

SUMMARY OF CONCLUSIONS

The following observations and conclusions were made from the analytical data obtained.

Montmorillonite is present as a mixed-layer mineral in the shales directly above and below the chert-bearing limestones and the limestones containing volcanic glass shards and is essentially absent in all other shales.

It is inferred that the montmorillonite in the shales directly above and below the chert-bearing limestones was formed by devitrification of volcanic ash.

Mixed-layer clay minerals were found to be present in nearly every sample. Chlorite-vermiculite was the most abundant of these

mixed-layer clay minerals and showed evidence in some cases of being regularly mixed.

The presence of chlorite and the mixed-layer clay of chlorite-vermiculite in the gray shales indicates that deposition of these shales probably took place in brackish water where reducing conditions were predominate.

The kaolinite in the red shales is either allogeneic or produced by the weathering of the sediments shortly after deposition.

Illite, chlorite, and the mixed-layer chlorite-vermiculite were found in all shales. Green, yellow, or buff colored shales showed variable amounts and usually smaller amounts of chlorite and chlorite-vermiculite than the gray shales.

A mixed-layer clay mineral of chlorite-illite and two non-clay minerals, quartz and calcite, were found in the clay size fraction of some of the shales. Calcite was found generally to be a major component of the clay size fraction of red shales. The amount of quartz present in the clay fraction of the shales showed a general tendency to decrease as the amount of chlorite increased and vice versa.

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CLAY MINERALOGY OF SOME OF THE PERMIAN SHALES

by

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The purpose of this investigation was to study all of the clay minerals present in some of the Permian shales in the Manhattan area and to see if a relationship might exist between the physical appearance of the shale and their clay mineral composition. The study was designed primarily to determine how montmorillonite was present in the shales directly above and below the chert-bearing limestones.

Samples were collected from some of the Permian shales of the Chase and Council Grove groups in the Manhattan area. The units sampled were the Blue Springs, Wymore and Havensville shales of the Chase group and the Speiser, Easley Creek, Hooser, Stearns and Florena shales of the Council Grove group. The type of samples collected was linear serial series.

The clay size material was separated from the shales by gravity sedimentation using standard sedimentation cylinders. Differential thermal data and X-ray diffraction data was obtained on the material in the clay size range.

From the differential thermal analysis and the X-ray diffraction analysis the following observations and conclusions were made.

Montmorillonite is present as a mixed-layer mineral in the shales directly above and below the chert-bearing limestones and the limestones containing volcanic glass shards and is essentially absent in all the other shales.

It is inferred that the montmorillonite in the shales directly above and below the chert-bearing limestones was formed by devitrification of volcanic ash.

Mixed-layer clay minerals were found to be present in nearly every

sample. Chlorite-vermiculite was the most abundant of these mixed-layer clay minerals and showed evidence in some cases of being regularly mixed.

The presence of chlorite and the mixed-layer clay of chlorite-vermiculite in the gray shales indicates that deposition of these shales probably took place in brackish water where reducing conditions were predominate.

The kaolinite in the red shales is either allogeneic or produced by the weathering of the sediments shortly after deposition.

Illite, chlorite, and the mixed-layer chlorite-vermiculite were found in all shales. Green, yellow, or buff colored shales showed variable amounts and usually smaller amounts of chlorite and chlorite-vermiculite than the gray shales.

A mixed-layer clay mineral of chlorite-illite and two non-clay minerals, quartz and calcite, were found in the clay size fraction of some of the shales. Calcite was found generally to be a major component of the clay fraction of the red shales. The amount of quartz present in the clay fraction of the shales showed a general tendency to decrease as the amount of chlorite increased and vice versa.

